PATENT SPECIFICATION (11) 1400529

(54) A PROCESS FOR THE CATALYTIC CONVERSION OF
HYDROCARBON CHLORIDES

(71) We, BAYER AKTIENGESELL-SCHAFT, a body corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to a process for the catalytic conversion of hydrocarbon chlorides. In particular, the present invention relates to a gaseous-phase process for the catalytic conversion of hydrocarbon chlorides into chlorine-free hydrocarbons and hydrogen chloride.

Chlorinated hydrocarbons are formed as by-products of numerous chemical processes; in general these by-products have no further use and they are destroyed but their destruction, e.g. by burning, involves considerable technical difficulties and great expense. In many cases it is difficult to destroy the hydrocarbon chlorides, particularly in view of the hydrogen chloride thereby evolved, whilst at the same time observing the regulations concerning spent air and waste water. Thus, the main problem in destroying and disposing of these compounds lies in their chlorine content. It is known that chlorine can quantitatively be removed from halogen compounds by conducting the halogen compounds together with hydrogen over a nickel catalyst at 700°C in the presence of ammonia (Angewandte Chemie, vol. 51, pg. 892 (1938)). In this process 1 mol of ammonia is required for each mol of hydrogen chloride which forms; the hydrogen chloride then being chemically reacted to ammonium chloride. Hence, this process involves considerable technical outlay.

The difficulties entailed in destroying hydrocarbon chlorides can be overcome according to the process of the present invention by converting the hydrocarbon chlorides into chlorine-free hydrocarbons and hydrogen chloride gas. The hydrocarbons can then be destroyed without any problem, for example by burning. The hydrogen chloride gas can be collected for example by dissolution in water and employed as an aqueous hydrochloric acid for very many different purposes.

Accordingly, the present invention provides a process for the catalytic conversion of hydrocarbon chlorides into chlorine-free hydrocarbons, wherein a hydrocarbon chloride is reacted in the gaseous phase at a temperature in the range of from 50 to 500°C in the presence of hydrogen and in the presence of a rhodium-containing catalyst.

It was found that catalysts containing rhodium possess high activity for the above-mentioned reaction and that they have a long life period which is of decisive importance for the continuous technical performance of the process. During the reaction the chlorine contained in the hydrocarbon chloride is converted into hydrogen chloride and chlorine-free hydrocarbons are also formed. The latter may be saturated or unsaturated, aliphatic, cycloaliphatic or aromatic hydrocarbons.

The ratio of the hydrogen to hydrocarbon chloride required for the catalytic conversion can be varied within wide limits. For example, the hydrogen can be used in an amount which corresponds to from 0.1 to 100 atoms of hydrogen per atom of chlorine. For example, hydrogen can be employed in an amount which corresponds to from 1 to 10 atoms of hydrogen per atom of chlorine.

Hydrogen can also be used in an amount which corresponds to from 2 to 5 atoms of hydrogen per atom of chlorine. The process can be so carried out that the residual gas which is free of hydrogen chloride contains 1 to 80 mole % of hydrogen, more particularly 20 to 60 mol%. It may be advantageous to recycle the non-reacted hydrogen either completely or partially into the reaction after separation of hydrogen chloride and possibly also after separation of chlorine-free hydrocarbons.
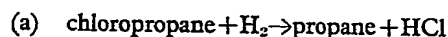
The catalytic conversion of the hydrocarbon

chlorides can be carried out by means of overall reactions in which larger amounts of hydrogen are reacted, e.g. according to the equation

5   dichloropropane$+2H_2\rightarrow$propane$+2HCl$
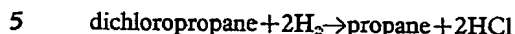
The conversion can also be carried out by means of overall reactions in which, in the overall stoichiometric reaction, no hydrogen is consumed, e.g.
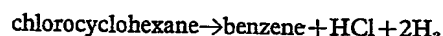
10   chloropropane$\rightarrow$propylene$+HCl$

which can be divided into

(a)   chloropropane$+H_2\rightarrow$propane$+HCl$

and

(b)   propane$\rightarrow$propylene$+H_2$
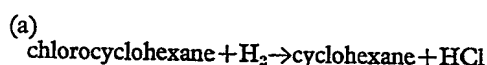
15   In these cases it may prove advantageous to employ small amounts of hydrogen per atom of chlorine, e.g. 0.1 to 2 atoms of hydrogen. The conversion can also be carried out by reactions in which, in the overall stoichio-

20 metric reaction, hydrogen is produced, e.g. according to the equation

chlorocyclohexane$\rightarrow$benzene$+HCl+2H_2$

which can be divided into

(a)
chlorocyclohexane$+H_2\rightarrow$cyclohexane$+HCl$

(b)

25   cyclohexane$\rightarrow$benzene$+3H_2$

In this case it may also be advantageous to work with small amounts of hydrogen, for example, using an amount of hydrogen which corresponds to from 0.1 to 10 atoms of hydro-

30 gen per atom of chlorine. The process may of course also be performed so that any hydrogen which may be formed during the catalytic conversion is employed for the subsequent reaction.

35   The most varied hydrocarbon chlorides can be reacted according to the invention. The hydrocarbon chlorides can contain one or more chlorine atoms in the molecule. The hydrocarbon chlorides can contain one or more

40 hydrogen atoms as well as the elements C and Cl; however, compounds which only contain carbon and chlorine are also suitable. For example compounds suitable for the reaction include those having an elementary

45 analysis which shows that they consist of carbon and chlorine. Other suitable compounds include those consisting of carbon, chlorine and hydrogen having an organically bound chlorine-content of from 10 to 90%

50 by weight.

In the process according to the invention it is possible to use, for example, hydrocarbon chlorides containing 1 to 30 carbon atoms in which there is at least 1 chlorine atom per molecule.   55

Compounds with up to 30 carbon atoms include: saturated or unsaturated, straight-chain or branched-chain, aliphatic and saturated or unsaturated, cycloaliphatic hydrocarbons, optionally substituted by one or   60 several straight-chain or branched chain, saturated or unsaturated aliphatic radicals as well as aromatic hydrocarbons, optionally substituted by one or more straight-chain or branched chain alkyl or alkenyl radicals, one   65 or more H atoms of said hydrocarbons being replaced by chlorine.

The following hydrocarbon chlorides are mentioned as examples of starting compounds which can be used in the reaction according   70 to the invention:
monochloromethane, dichloromethane, trichloromethane, tetrachloromethane, monochloroethane, dichloroethane, trichloroethane, tetrachloroethane, pentachloroethane, hexa-   75 chloroethane, monochloroethylene, dichloroethylene, trichloroethylene, tetrachloroethylene, monochloropropane, dichloropropane, trichloropropane, tetrachloropropane, pentachloropropane, hexachloropropane,   80 heptachloropropane, octachloropropane, monochloropropylene, dichloropropylene, trichloropropylene, tetrachloropropylene, pentachloropropylene, hexachloropropylene, monochlorobutane, dichlorobutane, trichlorobutane, tetra-   85 chlorobutane, monochlorobutylene, dichlorobutylene, trichlorobutylene, tetrachlorobutylene, chloropentane, dichloropentane, chlorocyclopentane, dichlorocyclopentane, tetrachloropentane, chlorohexane, dichloro-   90 hexane, tetrachlorohexane, chlorohexene, chlorocyclohexane, dichlorocyclohexane, chlorocyclohexene, chlorooctane, chlorohexadecane, chlorinated C_{20}-hydrocarbons, such as 2 - chloro - 2 - methyl - nonodecane, chlorin-   95 ated C_{30}-hydrocarbons, such as chloro-isotriacontane, chlorobenzene, vinyl-chlorobenzene, dichlorobenzene, trichlorobenzene, tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, chlorotoluene, dichlorotoluene, tri-   100 chlorotoluene, chloroxylene, dichloroxylene, tetrachloroxylene, chloronaphthalene, diethylchloronaphthalene, chloromethylnaphthalene, benzyl chloride and phenyl-stearylchloride; and mixtures of such hydrocarbon chlorides.   105 In particular, mixtures of aliphatic chlorinated hydrocarbons having from 8 to 20 C atoms and/or mixtures of chlorinated aromatic hydrocarbons having from 8 to 20 atoms can be used.   110

During the reaction according to the invention the following hydrocarbons can be formed for example:
methane, ethane, ethylene, propane, propylene, butane, butylene, pentane, pentene,   115

cyclopentane, hexane, hexene, cyclohexane, heptane, heptene, octane, decane, C_{20}-hydrocarbons, such as, 2-methylnonadecane, C_{30}-hydrocarbons, such as, isotriacontane, benzene, toluene, styrene, naphthalene, heptadecanylbenzene, as well as hydrocarbon mixtures, for example, mixtures of aliphatic hydrocarbons having from 8 to 20 C atoms and/or mixtures of aromatic hydrocarbons having from 8 to 20 C atoms.

Pure hydrocarbon chlorides can be used in the reaction; however, work can be carried out with mixtures of the most different hydrocarbon chlorides.

The reaction can be carried out at a temperature in the range of from 50 to 500°C and, in particular the reaction can be carried out at temperatures of 100 to 400°C. It may be advantageous to perform the reaction in the temperature range of 150 to 350°C. The reaction can be carried out at normal, reduced or elevated pressure. Suitable pressures are, for example, 1 to 10 pressures gauge. Both pressure and temperature should be selected so that the starting mixture is in the gaseous phase at the start of the reaction. It is advantageous to carry out the reaction in the absence of oxygen. The starting hydrogen can be pure hydrogen, e.g. electrolytic hydrogen. However, mixtures of hydrogen with inert gases, for example, methane, argon and nitrogen can be used. e.g. hydrogen fractions which are recovered during the catalytic or thermal conversions of mineral oils.

Hydrogen can also be used which contains hydrocarbon chloride. The starting materials can be used in anhydrous form; however, products can also be used which contain small amounts of water, for example, in a quantity corresponding to the solubility of water at room temperature in the hydrocarbon chlorides employed. In order to avoid corrosion when carrying out the process on a large scale it is expedient to use anhydrous or almost anhydrous starting materials.

Suitable catalysts are those which contain at least a catalytic amount of rhodium in the form of a rhodium compound or as the metal. It is advantageous to employ the rhodium applied to a carrier. Carrier catalysts can be used which contain the rhodium in the form of compounds or as metal. Rhodium can be contained as the sole of catalytically active component in the catalyst, but catalysts can also be used which contain other metals or metal compounds as well as rhodium, for example, the metals or compounds of the elements palladium, platinum, ruthenium, iridium, iron, cobalt, nickel, copper, gold, vanadium, chromium, molybdenum and tungsten. The catalyst can also contain compounds of different elements, for example salts or hydroxides or carboxylates, such as, acetates, of the alkali metals and alkaline-earth metals, such as salts or oxides of aluminium,

boron and titanium. For the production of catalysts the most varied carrier materials can be used, for example, aluminium oxide, silicic acid, aluminium silicate, spinel, active charcoal and titanium dioxide. It is advantageous to use carriers which are chemically resistant towards halogen hydracids. The carriers can possess the most varied physical properties. For example, the inner surface area can be between 1 and 500 m^2/g.

The most varied rhodium compounds can be used as starting materials, for the production of catalysts containing rhodium, for example, rhodium - (III) - oxide hydrate, potassium hexachlororhodiate, ammonium hexachlororhodiate, rhodium oxide hydrate, rhodium - III - acetate, rhodium - (III) - chloride hydrate, rhodium sulphate, rhodium phosphate and sodium rhodium nitrite. In many cases it is advantageous to start with the water-soluble and generally accessible rhodium-III-chloride hydrate. When halogen-free rhodium compounds are used as starting materials for the production of the catalysts this rhodium-III-chloride hydrate can, for example, be first reacted in an aqueous solution with sodium hydroxide, a rhodium oxide hydrate is thereby precipitated which, after washing to remove water-soluble halogen compounds, can be reacted with acetic acid to form a solution of rhodium acetate in acetic acid.

The production of the rhodium-containing catalysts can be carried out in very many ways. For example, aqueous solution of rhodium-III-chloride hydrate or acetic or aqueous solutions of rhodium acetate can be applied by soaking to the carrier and then dried. The resulting catalysts can be used directly for the reaction or they can be first reacted to form other compounds by further chemical or thermal treatment. For example, after application of rhodium chloride hydrate by soaking and subsequent drying, a solution of alkali metal hydroxide, e.g. sodium hydroxide or potassium hydroxide, can be applied by soaking, and conversion to the oxide hydrate of rhodium can be achieved on the carrier. The resulting catalysts can be freed of chlorine compounds by washing with water, after which the catalyst is dried and is then ready for use in the reaction. After application of a rhodium acetate solution by soaking and subsequent drying by heating, the rhodium acetate can be decomposed and a catalyst is obtained comprising rhodium oxide on the carrier. In the event that rhodium be introduced into the reaction as rhodium metal, the rhodium compounds applied by soaking to the carrier of the compounds, which are produced by chemical or thermal treatment, for example, rhodium chloride, rhodium oxide, rhodium oxide hydrate and rhodium acetate can be reduced to the metal by the action of reducing agents, e.g. by treat-

ment with hydrogen. The catalysts which contain rhodium compounds can also be introduced into the reaction and the reduction to rhodium metal carried out in the reactor during the subsequent reaction with hydrogen. Should the catalysts contain other metals or metal compounds in addition to rhodium, the production can be carried out so that solutions of rhodium salts and other metal salts, e.g. sodium palladium chloride, tetrachloroauric acid, hexachloro platinic acid, iron-III-chloride, chromic acid, sodium vanadate, sodium tungstate, potassium molybdate are applied by soaking to the carrier and after drying the resulting catalysts are used as such or first converted into other compounds, e.g., oxides or hydroxides by thermal treatment or chemical reaction. By treatment with reducing agents, e.g. hydrogen, a partial or complete conversion to the metals can be performed prior to introduction into the reaction or during the reaction. Finally, it is possible to first apply to the carrier metal compounds which do not contain rhodium, to convert these compounds, if desired, by thermal treatment or by chemical reaction and then in a second stage to apply the rhodium compounds by soaking.

The rhodium content in the catalyst can be varied within wide limits. It can be for example from 0.01 to 5% by weight.

Rhodium contents of from 0.1 to 1% by weight are particularly suitable. Should additions of other metals or metal compounds be made to the rhodium, then for example, from 0.1 to 10 parts of the added metals or metal compounds can be employed per part by weight of rhodium (calculated as metal).

It may be advantageous to carry out the reaction of hydrocarbon chlorides with hydrogen to produce hydrocarbons and hydrocarbon halides in tubular reactors and to conduct the gaseous starting materials over the catalyst which is stationary in the reaction tubes. The reaction tubes can, for example, have lengths of 2 to 8 m and inner diameters of from 20 to 50 mm. The catalysts can have a particle size of, for example, 3 to 8 mm. When using tubular reactors the reaction heat can be drawn off in conventional manner, e.g. by boiling pressure water, and recovered in the form of high pressure-steam.

The process can also be carried out in tubular reactors and the reaction heat only partly conducted off, e.g. by means of air coolers, so that the reactor exit has a higher temperature than the reactor entrance. The temperature of the reactor entry can, for example, be 150°C and the exit temperature 350°C.

In continuous commercial production it is possible when working with liquid hydrocarbon halides to introduce them into an evaporator and to conduct hydrogen at a suitable evaporator temperature through the liquid hydrocarbon halides. The mixture of hydrogen and hydrocarbon halides can then be heated up to the reaction temperature and conducted over the catalyst at this temperature. The gaseous reaction product can be cooled, for example to a temperature of from 20 to 50°C. The reaction product contains the non-reacted hydrogen, the formed hydrocarbon and the formed hydrogen chloride. In cases where the hydrogen also contains inert gases, such as, methane or nitrogen, these are also present in the reaction product. The reaction can be carried out so that the hydrocarbon halides are completely reacted in a straight throughput. It may be advantageous to select the conditions such that the hydrocarbon halides are only partly reacted in a straight throughput e.g. to 70 to 90%. In this case the non-reacted hydrocarbon halides can be separated from the reaction product. The process can be so carried out for example that after cooling of the reaction gas and compression, the non-reacted hydrocarbon chlorides are separated off in the liquid phase and then recycled to the reaction, so that eventually all the hydrocarbon chlorides are completely converted into chlorine-free hydrocarbons and hydrogen chloride. However, after cooling and optionally after compression it is also possible to wash the non-reacted hydrocarbon chlorides in counter-current out of the reaction gases by washing with an organic solvent and upon regeneration of the washing agent, e.g. by distillation, to recover the non-reacted hydrocarbon chlorides and to recycle them into the reaction.

The reaction gas of the process according to the invention contains, optionally after separation of any non-reacted hydrocarbon chloride, hydrogen, the chlorine-free hydrocarbons and hydrogen chloride. This gas can either be employed for chemical reactions, in which hydrogen chloride is required, or the hydrogen chloride can be removed in conventional manner, for example by washing, e.g. with water, to produce a residual gas consisting of hydrogen and chlorine-free hydrocarbon for further use or combustion.

During the reaction of the hydrocarbon chlorides with hydrogen in the process according to the invention, small amounts of hydrocarbon chlorides are produced as by-products which possess a smaller number of chlorine atoms per molecule than the starting material. These chlorinated hydrocarbons may be separated from the reaction gas and recycled to the reaction so that chlorine-free hydrocarbons are obtained in the end but in some cases this is difficult and involves considerable technical outlay. In these cases it may be more expedient by suitable selection of the working conditions, such as pressure, temperature, hydrogen/hydrocarbon chloride ratio and throughput, to control the reaction so that these hydrocarbon chlorides, which have a

lower number of chlorine atoms per molecule than the starting material, are not produced.

In cases in which chlorinated hydrocarbons, which possess fewer chlorine atoms per mole-
cule than the starting material, are not pro-
duced, then the chlorinated hydrocarbons em-
ployed can be entirely or partially reacted.
Where incomplete conversion is achieved in a straight throughput, the non-reacted hydro-
carbon chlorides can be separated by a con-
ventional technique from the reaction gas and recycled to the reaction and thus completely reacted in the end. Where separation of the non-reacted hydrocarbon chlorides is difficult or technically complicated, then it may be expedient to select such working conditions which will result in a complete reaction to chlorine-free hydrocarbons in a straight throughput.

It may be advantageous to activate the carriers used for the reaction prior to the production of the catalysts, for example by treatment with aqueous or gaseous hydrogen chloride. It may further be advantageous to activate the carriers or the catalysts after application of the rhodium by treatment with aqueous or dry hydrogen chloride and/or by treatment with alkali or alkaline-earth metal hydroxides or alkali or alkaline earth metal salts. Before reacting with hydrocarbon halides, the catalysts can be activated by dry-
ing and/or treatment with hydrogen and/or treatment with mixtures of hydrogen and hydrogen chloride.

When initiating the reaction the catalyst which contains the rhodium as the metal or metal compound, can be introduced into the reactor, freed of oxygen by rinsing with nitrogen; the catalyst is then heated in the hydrogen stream to the reaction temperature or to a temperature above the reaction tem-
perature, e.g. to temperatures of 150 to 500°C, then adjusted to the reaction tem-
perature in the hydrogen stream and the re-
action can then be started by the addition of hydrocarbon chlorides. Prior to introduc-
tion the hydrocarbon chlorides can be freed of dissolved oxygen and/or any water which may be present. For example, any water can be azeotropically removed in a distillation column and oxygen-free and anhydrous hydro-
carbon chloride removed from the column as a branch stream and introduced into the re-
action.

When working in the absence of water or under practically anhydrous conditions it is possible to use normal steel as the reactor material, since in the presence of dry hydro-
gen chloride no corrosion takes place.

The process of the invention is distinguished by the use of a particularly active catalyst which also has a long catalytic life-period, a fact of importance when conducting the pro-
cess on a large scale. The process of the invention can be so executed that no carbon

deposition or practically no carbon deposition occurs on the catalyst. By this means a long life-period of the catalyst can be achieved and frequent regeneration of the catalyst which is undesirable from a technical point of view can be avoided.

The invention is illustrated by the follow-
ing Examples.

Example 1

A rhodium-containing catalyst was manu-
factured as follows:

An aqueous solution of rhodium-III-
chloride hydrate was applied by soaking to aluminium oxide having a particle size of approx. 5 mm. The resulting treated aluminium oxide carrier was dried and sub-
jected to a hydrogen stream at 250°C for 2 hours. The finished catalyst contained 1% by wt. of rhodium on the aluminium oxide carrier. 1 l of the catalyst was placed in a reaction tube of 25 mm internal diameter and 2.5 m length. 1 mol of dichloropropane and 3.5 mol of hydrogen were conducted over the catalyst hourly at normal pressure and at a temperature of 180°C. A complete conver-
sion was obtained according to the equation

$$\text{dichloropropane} + 2H_2 \rightarrow \text{propane} + 2HCl$$
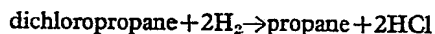
The test was carried out over a period of 400 hours. During this test period no sub-
sidence of catalytic activity was observed so that even at the end of this test complete re-
action to propane and hydrogen chloride took place.

Example 2

The process was carried out as described in Example 1, except that a mixture of 4 mol of 1,2-dichloropropane and 14 mol of hydrogen were conducted hourly over the catalyst. 95% of the used dichloropropane were reacted to propane and HCl, 5% of the dichloropropane were not reacted. Mono-
chlorinated hydrocarbons were not formed. The non-reacted dichloropropane was separ-
ated off from the reaction gas and recycled to the reaction.

Example 3

The process was performed as described in Example 1, except that a catalyst was used which contains 0.1% by wt. of rhodium and the reaction was carried out at a temperature of 250°C instead of 180°C. 98% of the 1,2-
dichloropropane employed reacted to form a mixture of propylene and propane and HCl. 2% of the dichloropropane did not react and monochlorinated hydrocarbons were not formed.

Example 4

The process was performed as described in Example 1, except that 1 mol of chloro-

benzene and 10 mol of hydrogen were conducted hourly over the catalyst. A quantitative conversion to cyclohexane and hydrogen chloride took place.

Example 5

The process was carried out as described in Example 4, except that 1 mol of carbon tetrachloride was used instead of the chlorobenzene. A quantitative reaction to methane and hydrogen chloride was achieved.

The same results were obtained when, instead of carbon tetrachloride, trichloromethane, dichloromethane or monochloromethane were used.

Example 6

The process was carried out as described in Example 4, except that 1 mol of dichlorobutene was used instead of chlorobenzene. A complete reaction to n-butane and HCl took place.

Example 7

The process was carried out as described in Example 1, except that the following catalysts were used:

a) 0.9% by wt. of rhodium and 0.1% palladium on aluminium oxide;
b) 0.9% by wt. of rhodium and 0.1% platinum on aluminium oxide;
c) 0.9% by wt. of rhodium and 0.1% gold on aluminium oxide;
d) 0.9% by wt. of rhodium and 0.1% nickel on aluminium oxide;
e) 1% by wt. of rhodium on lithium aluminium spinel.

The same values were obtained as in Example 1.

Example 8

The process was carried out as described in Example 3, except that the reaction was carried out at 350°C. The dichloropropane employed was completely converted to HCl and a mixture of propylene and propane in a ratio of about 2:1.

Example 9

The process was carried out as described in Example 8 except that a catalyst was used which contained 0.1% of rhodium on activated charcoal (particle size 4 mm). The dichloropropane employed was completely converted to HCl and a mixture of propylene and propane. The test was carried out over a period of 1000 hours. During the test period no subsidence of catalyst activity was detected so that a complete reaction took place even at the end of the test.

WHAT WE CLAIM IS:—

1. A process for the catalytic conversion of hydrocarbon chlorides into chlorine-free hydrocarbons, wherein a hydrocarbon chloride is reacted in the gaseous phase at a temperature in the range of from 50 to 500°C in the presence of hydrogen and in the presence of a rhodium-containing catalyst.

2. A process as claimed in claim 1, wherein the hydrocarbon chloride consists of carbon and chlorine.

3. A process as claimed in claim 1, wherein the hydrocarbon chloride consists of carbon, chlorine and hydrogen and has an organically bound chlorine content of from 10 to 90% by weight.

4. A process as claimed in any of claims 1 to 3, wherein the hydrocarbon chloride has from 1 to 30 carbon atoms.

5. A process as claimed in any of claims 1 to 4, wherein the hydrocarbon chloride is a saturated or unsaturated, straight-chain or branched chain, aliphatic or cycloaliphatic saturated or unsaturated hydrocarbon containing up to 30 carbon atoms, optionally substituted by one or more straight-chain or branched chain saturated or unsaturated aliphatic radical, or an aromatic hydrocarbon, optionally substituted by one or more straight-chain or branched-chain alkyl or alkenyl radicals wherein one or more hydrogen atoms of the hydrocarbons are replaced by chlorine.

6. A process as claimed in any of claims 1 to 5, wherein a mixture of hydrocarbon chlorides is used.

7. A process as claimed in claim 1, wherein the hydrocarbon chloride according to claims 1 to 5, characterised is 1,2-dichloropropane.

8. A process as claimed in any of claims 1 to 7, wherein from 0.1 to 100 atoms of hydrogen per atom of chlorine of the hydrocarbon chloride are used for the reaction.

9. A process as claimed in claim 8, wherein from 1 to 10 atoms of hydrogen per atom of chlorine of the hydrocarbon chloride are used for the reaction.

10. A process as claimed in claim 9, wherein 2 to 5 atoms of hydrogen per atom of chlorine of the hydrocarbon chloride are used for the reaction.

11. A process as claimed in any of claims 1 to 10, wherein after the separation of hydrogen chloride and optionally of chlorine-free hydrocarbons, the non-reacted hydrogen is completely or partially recycled to the reaction.

12. A process as claimed in any of claims 1 to 11, wherein rhodium in metal form is employed in the rhodium-containing catalyst.

13. A process as claimed in any of claims 1 to 11, wherein rhodium in the form of a rhodium compound is employed in the rhodium-containing catalyst.

14. A process as claimed in any of claims 1 to 13, wherein the catalyst is supported on a carrier.

15. A process as claimed in any of claims 1 to 14, wherein characterised the catalyst also

contains additions of metals or compounds thereof of the elements palladium, platinum, ruthenium, iridium, iron, cobalt, nickel, copper, gold, vanadium, chromium, molybdenum or tungsten.

16. A process as claimed in any of claims 1 to 15, wherein the catalyst also contains salts or hydroxides or carboxylates of the alkali metals or alkaline-earth metals, and/or salts or oxides of aluminium, boron or titanium.

17. A process as claimed in any of claims 1 to 16, wherein the catalyst contains from 0.01 to 5% by weight of rhodium as metal or in the form of a compound on the carrier.

18. A process as claimed in claim 17, wherein the catalyst contains 0.1 to 1% by weight of rhodium as metal or in the form of a compound on the carrier.

19. A process as claimed in any of claims 1 to 18, wherein from 0.1 to 10 parts of metal or metal compounds as additives are present for 1 part of rhodium, calculated as metal.

20. A process as claimed in any of claims 14 to 19, wherein the carrier is aluminium oxide, silicic acid, aluminium silicate, spinel, active charcoal or titanium dioxide.

21. A process as claimed in claim 20, wherein the carrier is activated charcoal.

22. A process as claimed in any of claims 1 to 21, wherein the reaction is carried out at a temperature in the range of 100 to 400°C.

23. A process as claimed in claim 22, wherein the reaction is carried out at a temperature in the range of 150 to 350°C.

24. A process as claimed in any of claims 1 to 23, wherein the reaction is performed in the absence of oxygen.

25. A process as claimed in any of claims 1 to 24, wherein anhydrous hydrocarbon chlorides are used as starting material for the reaction.

26. A process as claimed in claim 1, substantially as herein described with reference to any of the specific Examples.

27. Chlorine-free hydrocarbons produced by the process claimed in any of claims 1 to 26.

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